168. *High-temperature Thermal Decomposition of Ammonium Perchlorate.*

By A. K. Galwey and P. W. M. Jacobs.

The thermal decomposition of ammonium perchlorate at temperatures above about 350° c differs in several respects from that below this temperature. Reaction occurs by a different mechanism and here results in complete decomposition, whereas at low temperatures a residue of ammonium perchlorate always remains. Results for the kinetics of the high-temperature reaction have been analysed according to two alternative equations. Both fit the results well, but one of them, the "contracting-cube" formula, is preferred on theoretical grounds. A mechanism of the high-temperature reaction, consistent with that for the low-temperature reaction, is proposed.

Bircumshaw and Newman [1] made a brief study of the thermal decomposition of ammonium perchlorate in the temperature range 380—450°, sublimation of the reactant from the hot zone being prevented by a small pressure of inert gas. They noted that the reaction obeys the power law

$$p = kt^n \qquad (1)$$

where p is the pressure evolved in a constant-volume system in time t, and k and n are constants. The exponent n varied somewhat irregularly with temperature between 0·5 and 1·0. The reaction was deceleratory throughout and, in contrast to the low-temperature decomposition, resulted in complete decomposition of the salt.

After this work had been completed, Bircumshaw and Phillips [2] reported that between 300° and 380° the thermal decomposition of ammonium perchlorate gave irreproducible kinetic results under a wide variety of conditions, but reproducible ones from decompositions at 400—440°, velocity constants being dependent on the pressure of nitrogen used to suppress sublimation. The kinetics of the high-temperature decomposition fitted the equation $m^{2/3} = kt + c$, where m is the mass of salt undecomposed at time t, and k

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[1] Bircumshaw and Newman, *Proc. Roy. Soc.*, 1954, *A*, **227**, 115; 1955, *A*, **227**, 228.

[2] Bircumshaw and Phillips, *J.*, 1957, 4741.

and c are constants. Sublimation was prevented by a pressure of 20 cm. of nitrogen and an energy of activation of 73·4 ± 1·5 kcal./mole was obtained from the dependence of the rate constant (k) on temperature. Decomposition was virtually complete, and the gaseous products did not catalyse the reaction. Bircumshaw and Phillips suggested that the rate-determining step in the high-temperature reaction is the breakdown of the perchlorate ion because the energy of activation found was similar to that for the decomposition of pure potassium perchlorate (63·3 kcal./mole).[3]

The decomposition of ammonium perchlorate below 350° will be discussed in detail elsewhere[4] (see also refs. 1, 2, 3); the essential feature is that only intergranular material is decomposed, leaving a residue of salt chemically identical with the starting material.

EXPERIMENTAL

The apparatus used[4] to study the low-temperature decomposition is unsuitable at high temperatures because it was necessary to introduce an inert gas before each experiment and it was not possible to take a sufficient number of McLeod gauge readings to characterise the kinetics in runs lasting less than about 2 hr. Accordingly an apparatus was developed in which the pressure was measured by means of a glass spiral manometer. The pressure developed during decomposition in a constant-volume system was measured by the deflection (θ) of a light spot, reflected from a mirror mounted on the glass spiral on to a fixed scale. Calibration of this gauge, using a mercury manometer, showed that θ is proportional to the pressure difference across the gauge spiral and independent of the absolute pressure in the apparatus. Pressure readings could be taken every 10 sec., with an accuracy ±0·05 mm. Hg.

Preparation of materials will be described elsewhere.[4]

RESULTS

In the high-temperature decomposition region (above 350°) sublimation is fast. The behaviour of the salt at 350° in the presence and absence of inert gas is shown in Fig. 1. Curve A shows the variation of pressure with time observed for the decomposition of a fragment of a pellet dropped into the hot zone *in vacuo*. There was no residue, but substantial sublimation to the cooler walls above the reaction zone had occurred. In a similar run B with a pellet of nearly equal mass and the tube filled with 400 mm. of gas to suppress sublimation the fast initial pressure rise was followed by a slow rise in pressure. After 6 hours, while the slow reaction was still proceeding, only about one-third of the original weight of sample remained and no visible sublimation had occurred.

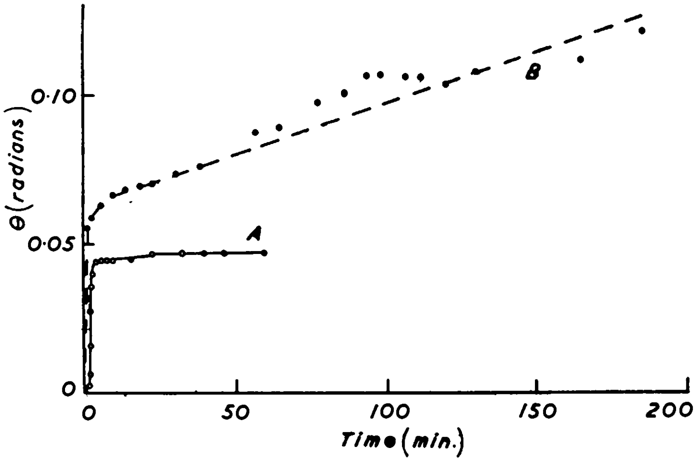

FIG. 1. *Pressure-time plots for the thermal decomposition of ammonium perchlorate pellet fragments* in vacuo (A) *and in* 400 *mm. of gas* (B).

As Bircumshaw and Phillips[2] report, the kinetics in the range 300—380° are irreproducible, though the low-temperature thermal decomposition *in vacuo* gave satisfactory rate constants up to 350°. Reactions in the presence of an inert gas were irreproducible at this temperature

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[3] Phillips, Thesis, Birmingham, 1953 (quoted in ref. 2).

[4] Galwey and Jacobs, to be published.

and probably consist of a mixture of the low-temperature decomposition and the reaction seen to occur when sublimation is suppressed, which will be called the high-temperature reaction.

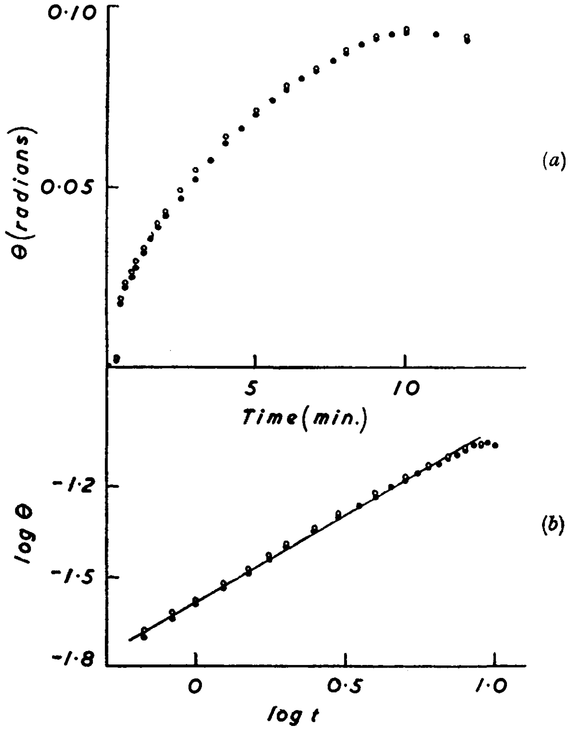


FIG. 2. *Thermal decomposition of pellet fragments of ammonium perchlorate at* 407°. *Full and open circles refer to two runs under identical conditions.*

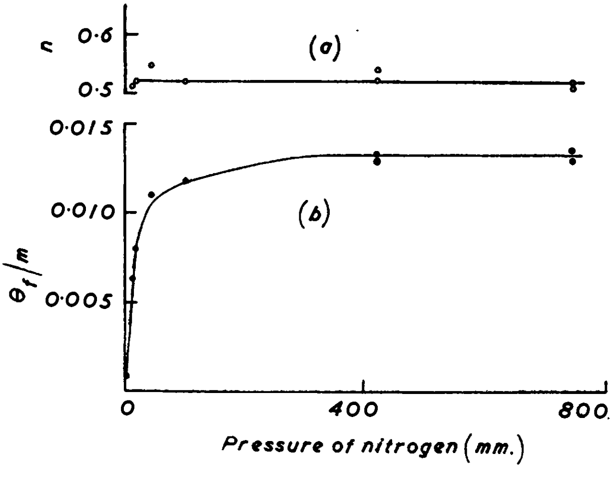


FIG. 3. *Thermal decomposition of ammonium perchlorate pellet fragments at* 407°. *Plots of* (*a*) *power-law index* (*n*) *and* (*b*) *ratio of final pressure to weight taken* (θ_f/m), *against the pressure of nitrogen used to suppress sublimation.*

Reproducibility.—Decompositions above 380° were reproducible. Three fragments of a single pellet of ammonium perchlorate, having very nearly equal masses, decomposed in 20 mm. of nitrogen under identical conditions to give virtually identical pressure–time curves. Two of these runs are represented in Fig. 2*a*, the third being omitted for clarity. These plots are deceleratory throughout, a characteristic feature of the high-temperature reaction. Fig. 2*b* shows the plot of log θ against log *t* for the same runs; the power law holds satisfactorily over the greater part of the reaction with $n = 0{\cdot}57$.

Variation of Pressure of Gas used to suppress Sublimation.—Successive fragments of a single pellet, of approximately equal masses, were decomposed at the same temperature under different initial pressures of dry nitrogen. The results, summarised in Fig. 3, show that the power law is obeyed, n being independent of the pressure of nitrogen, and that at low initial pressures, where substantial sublimation occurred, the ratio of the final pressure evolved as a result of decomposition (θ_f) to weight of sample (m) is small but increases rapidly with initial pressure of nitrogen. θ_f/m may be taken as a measure of the extent of reaction in this system where sublimation is fast; it is nearly independent of nitrogen pressure above about 300 mm., and 400 mm. was therefore used, unless otherwise stated.

Variation of Mass of Pellet.—Successive fragments of different mass of a single pellet were decomposed under identical conditions. The range of mass is limited by the sensitivity of the gauge at one extreme, and the largest mass which could be decomposed without causing condensation of water vapour, at the other. The results (Fig. 4) show that n varies somewhat with the mass decomposed, and that the rate constant is directly proportional to the mass decomposed. Attempts to fit the results to the Prout–Tompkins equation and to the unimolecular-decay law failed.

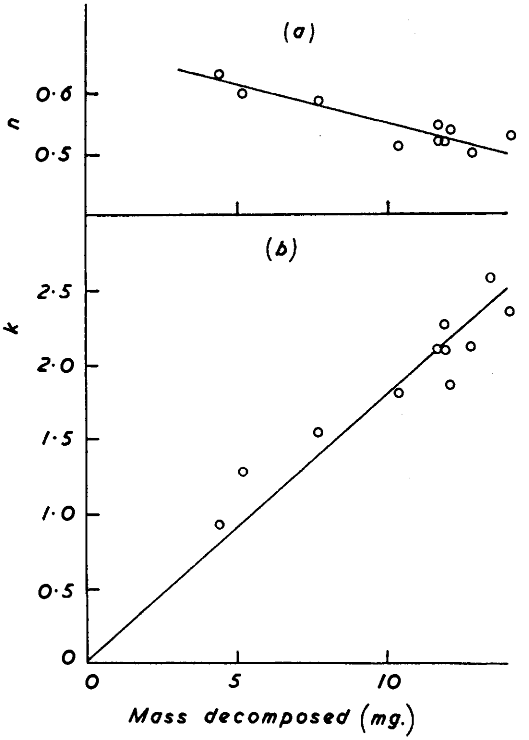


FIG. 4. *Thermal decomposition of ammonium perchlorate pellet fragments at 407° in 400 mm. of nitrogen. Variation of (a) power-law index (n) and (b) power-law rate constant (k) with mass decomposed.*

Variation of Temperature.—*Pellets.* Successive fragments of nearly equal mass of a single pellet were decomposed at different temperatures. All the pressure–time curves showed the characteristic shape illustrated in Fig. 2*a* and the power law fitted the results well over the whole reaction period in several runs. In certain runs, however, the index n was not constant throughout the reaction and two values, holding over different stages were found; a run showing this is in Fig. 5*a*. A plot of power-law indices against temperature of decomposition is shown in Fig. 5*b*. At lower temperatures, in the range studied, two different reaction periods are observed. Both indices increase with temperature, that for the initial period increasing more quickly than that for the decay period so that at higher temperature only a single value of the exponent is required.

Arrhenius energies of activation for the reaction were determined from plots of log (k/m) against $1/T°$ (K); log (k/m) was used since $k \propto m$, although the variation in mass for runs of this series was minimised. The plot for the initial region of reaction was too scattered to yield an energy of activation, but a satisfactory plot for the decay period was obtained. This is well represented by the equation:

$$\log (k/m) = 4{\cdot}96 - 17{,}540/(2{\cdot}303\boldsymbol{R}T)$$

which is valid for $0{\cdot}26 < \alpha < 0{\cdot}92$, m being expressed in mg. For three runs 400 mm. of oxygen was used instead of nitrogen. The rate constants and power law indices (Fig. 5*b*) are independent of which gas was used.

Single whole crystals. Single whole crystals, all prepared in a single recrystallisation, were decomposed under similar conditions to those used for pellets. The results fitted the power law although there was a perceptible curvature of the log p–log t plot, and results were less reproducible than those for pellet fragments. An Arrhenius plot was too scattered to yield an energy of activation. The values of n showed some scatter, but no systematic variation with temperature.

FIG. 5. *Thermal decomposition of ammonium perchlorate pellet fragments.* (*a*) *Pressure–time plot in the temperature region where two different values of the rate constant hold.* (*b*) *Variation of n with temperature of decomposition: broken line initial region; full line, final region. Open circles represent runs in an atmosphere of oxygen; other runs in nitrogen.*

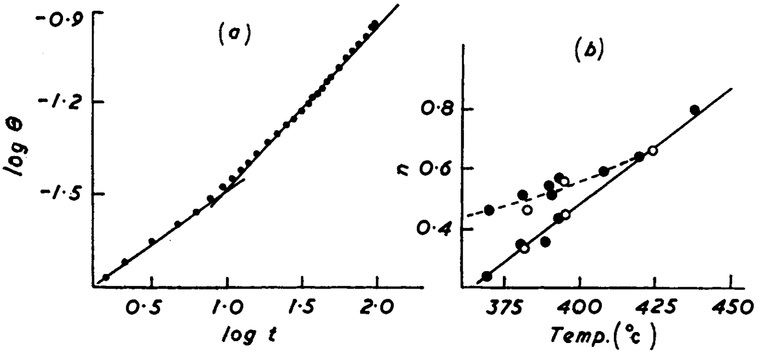


FIG. 6. *Thermal decomposition of ammonium perchlorate pellets previously decomposed at low temperatures. Plot of* log θ *versus* log t *showing three regions of reaction* (θ *in radians, t in minutes*).

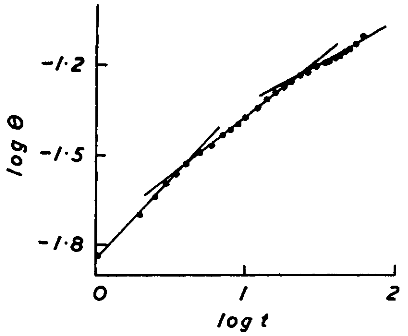
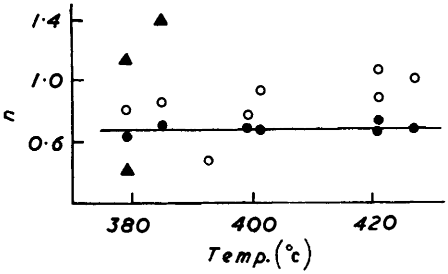


FIG. 7. *Thermal decomposition of ammonium perchlorate pellets previously decomposed at low temperatures*: ▲ initial region; ○ middle region; ● final region.



Residue from low-temperature thermal decompositions. Since reaction goes to completion in the high-temperature region it was clearly important to study, in this temperature range, the decomposition of residue left from the low-temperature thermal decomposition. Accordingly the materials from pellet fragments decomposed at 250—350° were reheated in the high-temperature range after being stored over fresh phosphoric oxide for not more than three days (usually not more than one day). Great care was taken to avoid mechanical damage and to limit contact with the atmosphere.

Here the power law was less satisfactory. In Fig. 6, three reaction regions are characterised by different rate constants and different exponents, though in some other runs of this series only two can be distinguished. Plots of the power-law indices for the middle (n_b) and final (n_c) regions of reaction show scatter, but no definite trend with temperature (Fig. 7). Arrhenius plots with rate constants for the middle (k_b) and final (k_c) regions were well represented by the equations:

$$\log (k_b/m) = 8{\cdot}67 - 30{,}000/(2{\cdot}303\boldsymbol{R}T), \quad 0{\cdot}15 < \alpha < 0{\cdot}40$$

and $$\log (k_c/m) = 8{\cdot}77 - 30{,}000/(2{\cdot}303\boldsymbol{R}T), \quad 0{\cdot}43 < \alpha < 0{\cdot}95.$$

DISCUSSION

The results for the high-temperature thermal decomposition of ammonium perchlorate fit the power law over a wide range of α. The fit is particularly satisfactory for the decomposition of "undecomposed" ammonium perchlorate; for several runs the equation holds over the complete reaction, the power-law index and rate constants being accurately reproducible. The power law, taken as an empirical equation, is useful for describing and systematising the experimental results. There are, however, theoretical objections to its use.

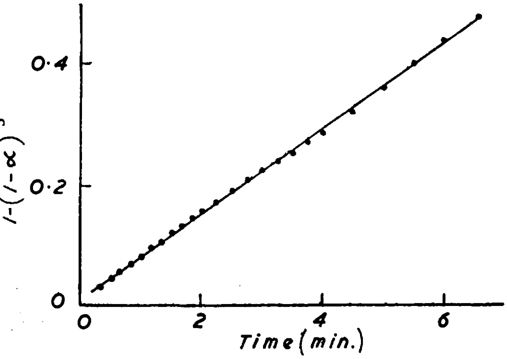


FIG. 8. *Thermal decomposition of a pellet of ammonium perchlorate: test of the contracting-cube formula.*

The power-law index varies with both the mass of fragment and the temperature of decomposition. The actual n–m and n–T relationships could not be expressed analytically owing to scatter (Figs. 4*a* and 5*b*) but the variability of n makes the significance of the derived energy of activation doubtful since the rate constants (given by log p when log $t = 0$) depend on the slope of the log p–log t plot, that is, on the value of n.

In several runs the power law shows more than one region of reaction, different values of n and k holding over successive ranges of α, the fractional decomposition, *e.g.*, Fig. 6. Also, the equation can only be regarded as fitting approximately the results for decomposition of whole crystals.

Finally, it is difficult to account for an exponent of less than unity in applying the power law to the decomposition of a solid. A value of $n < 1$ could be due to decomposition in the gas phase following sublimation of the solid, but the experimental evidence (Fig. 1) is that sublimation and decomposition are competing processes.

The first reaction, after the sample had been placed in the furnace (>350°), must involve the material which can decompose at low temperature, that is, the strained, intergranular regions of the lattice.[4] This leaves a residue consisting of a large number of blocks of material, adhering loosely at corners and edges. Their decomposition should obey an equation based on the recession of an interface parallel to the particle surface, that is, the contracting-cube formula:

$$kt = 1 - (1 - \alpha)^{\frac{1}{3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

To test this conclusion, the results were re-analysed by plotting $[1 - (1 - \alpha)^{\frac{1}{3}}]$ against t (Fig. 8). For pellets, decomposed and undecomposed, rate constants hold over the approximate range $0{\cdot}2 < \alpha < 0{\cdot}8$ and for crystals $0 < \alpha < 0{\cdot}7$. An Arrhenius plot for the decomposition of pellet fragments only, with rate constants derived from eqn. (2), yields an energy of activation of 38·8 kcal./mole.

Eqn. (2) requires that $1 - (1 - \alpha)^{\frac{1}{3}} = 0$ when $t = 0$, but the best experimental straight line did not always pass through the origin. This could be due either to initial rapid decomposition (the low-temperature reaction) or to a finite heating time or to a combination of both factors.

A composite Arrhenius plot for rate constants found by using eqn. (2) for the thermal decomposition of fragments of undecomposed ammonium perchlorate, fragments of ammonium perchlorate pellet which has undergone low temperature thermal decomposition, and whole single crystals of ammonium perchlorate, is shown in Fig. 9. The line gives the best fit for decomposition of fragments of undecomposed pellet, the plot for this series showing the least scatter of the three materials investigated. All the points lie reasonably close to the single straight line. Thus a *single* kinetic equation is obeyed over a large fraction of the decomposition for all three forms. The difficulty of theoretically accounting for the variation of power-law index with fragment mass and temperature does not arise with the contracting-cube law.

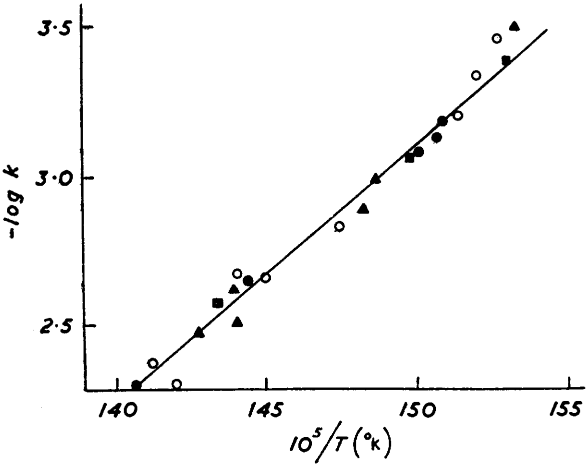


FIG. 9. *Arrhenius plot for the thermal decomposition of ammonium perchlorate. Fragments of a pellet of normal salt in nitrogen* (●) *and in oxygen* (■). ▲, *Pellet fragments previously decomposed at low temperatures*; ○, *single whole crystals.*

Since reaction above about 380° goes to completion for all three forms and the kinetic equations obeyed in the high- and the low-temperature range are quite different, different processes must control the rate.

Two possible reaction mechanisms are consistent with the contracting-cube model: (i) evaporation of an ion-pair followed by gas-phase decomposition of the ammonium perchlorate; (ii) proton transfer on the solid surface giving ammonia and perchloric acid.

In the high-temperature range, decomposition and sublimation probably compete since ammonium perchlorate can sublime unchanged *in vacuo*; the decomposition observed (Fig. 1) under these conditions can be attributed to the low-temperature reaction (which is independent of sublimation in the low-temperature range [1]). The mechanism by which ammonium perchlorate sublimes has not been established experimentally, but the volatile species in sublimation is probably an ion-pair formed as a result of the powerful proton-donating power of perchloric acid and stabilised by hydrogen-bonding. Ammonium salts of weaker acids sublime through dissociation (*e.g.*, $NH_4Cl \longrightarrow NH_3 + HCl$) but this may not occur with the ammonium salt of so strong an acid. The increased stability of perchloric acid to heat resulting from hydration gives further evidence for the existence of complexes of the acid capable of existence as gases, since the pure acid decomposes at 92° whereas an acid of composition $HClO_4,2H_2O$ distils at 203°.[5]

Energies of activation for sublimation and decomposition can be compared only if derived by use of the same kinetic equation or referred specifically to the same process (*e.g.*, propagation of an interface). Bircumshaw and Phillips[2] found the energy of activation for the sublimation to be $21{\cdot}5 \pm 2{\cdot}78$ kcal./mole using rate constants deduced from the equation $dm/dt = k$, which is the power law with an index of unity. This value cannot be compared with results for decomposition of fragments of fresh pellets since the power-law index varies systematically with temperature. However, comparison may be made with the energy of activation (30 kcal./mole) deduced from the power-law rate-constants found for the middle region of reaction of " decomposed " pellets where the exponent is approximately 0·9 and does not vary systematically with temperature. The large difference between the two energies of activation implies that different rate-determining steps operate in sublimation and high-temperature decomposition.

We suggest that the rate-determining step for the high-temperature thermal decomposition is a proton-transfer on the surface of the solid followed by oxidation of the ammonia gas by radicals resulting from the decomposition of perchloric acid. The mechanism of decomposition of perchloric acid has not yet been established, though the liquid decomposes below 100°, a reaction attributed[5] to the instability of the anhydride Cl_2O_7. It seems probable that perchloric acid should undergo fast decomposition at these temperatures, generating oxygen atoms which then oxidise the ammonia:

$$2HClO_4 \longrightarrow H_2O + Cl_2O_7 \qquad (3)$$

$$Cl_2O_7 \longrightarrow 2Cl_2 + 7O_2 \qquad (4)$$

$$4NH_3 + 5O_2 \longrightarrow 6H_2O + 4NO \qquad (5)$$

Reaction (4) is probably a chain reaction involving ClO_4, ClO_3, ClO_2, ClO, Cl, and O as intermediates.[6,7] The mechanism for the homogeneous oxidation of ammonia by molecular oxygen is not established in detail but the reaction is slow below 500°,[8] so that the oxidation of ammonia at these temperatures must be by atomic oxygen, from the decomposition of Cl_2O_7. This scheme accounts for the major products found by Dodé[9] who represented the overall reaction by

$$2NH_4ClO_4 \longrightarrow 4H_2O + 2NO + O_2 + Cl_2$$

The appearance of nitrosyl chloride and nitrogen as minor products is accounted for by the reaction of NO with Cl and the combination of N atoms [formed in eqn. (5)], respectively. The details of the reaction cannot yet be established, but our scheme accounts for the products and is consistent with known facts.

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IMPERIAL COLLEGE, LONDON, S.W.7. [*Received, September 8th*, 1958.]

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[5] Ephraim, " Inorganic Chemistry," 5th Edn., Gurney and Jackson, London, 1948, p. 389.
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[7] Schumacher and Stieger, *Z. phys. Chem.*, 1930, *B*, **7**, 363.
[8] Stephens and Pease, *J. Amer. Chem. Soc.*, 1950, **72**, 1188; 1952, **74**, 3480.
[9] Dodé, *Bull. Soc. chim. France*, 1938, **5**, 170.